

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
19.11.1997 Bulletin 1997/47

(21) Application number: 97107518.9

(22) Date of filing: 07.05.1997

(51) Int. Cl.⁶: G01N 21/35

REÇU LE

12 MAI 2004

Rép.:

(84) Designated Contracting States:
DE FR GB

(30) Priority: 13.05.1996 US 645104

(71) Applicant:
Perstorp Analytical, Inc.
Silver Spring, Maryland 20904 (US)

(72) Inventors:
• Chen, Xiaolin
Beltsville, Maryland 20705 (US)
• Monfre, Stephen L.
Plainville, Massachusetts 02762 (US)

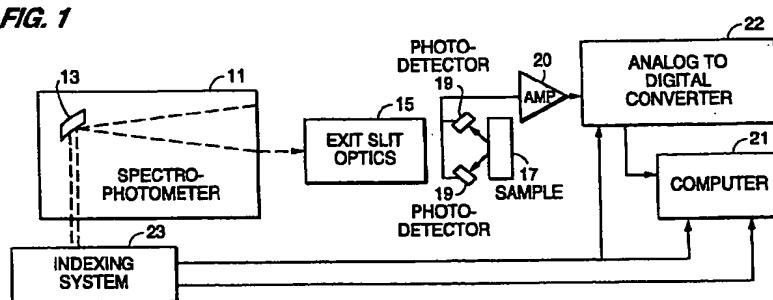
(74) Representative:
DIEHL GLAESER HILTL & PARTNER
Patentanwälte
Königstrasse 28
22767 Hamburg (DE)

(54) System for identifying materials by NIR spectrometry

(57) In a method for identifying an unknown product a library of absorbance spectra of known products is measured and stored in a library. A quick search using clustering techniques is conducted to narrow the search to a few products, followed by an exhaustive search of the spectra of the few products. More specifically, principal component analysis is applied to the absorbance spectra to generate product score vectors extending into principal component inside model space which are divided into clusters and subclusters in accordance with their relative proximity. Hyperspheres are constructed around each vector and an envelope is constructed to enclose each cluster surrounding the hyperspheres within the cluster. The absorbance spectrum of the unknown product to be identified is measured and an unknown product score vector is determined from the

unknown product spectrum projecting in principal component inside model space of the clusters. It is determined whether or not the unknown product score vector falls within one of the envelopes and if so the product score vector is projected into the principal component inside model space of that cluster and it is determined whether or not the unknown product score vector falls within any of the subclusters divided from the cluster. This process is repeated until the unknown product score vector is found to lie in a cluster which is not further subdivided. In this manner, the search is narrowed to a few products. An exhaustive search is then carried out to match the spectrum of the unknown product with the spectra of the known products corresponding to the undivided subcluster.

FIG. 1



BEST AVAILABLE COPY

Description**Background of the Invention**

5 This invention relates to a system for identifying materials and, more particularly, to a system making use of infrared analysis to match an unknown material with one of a large number of known materials and in this manner identify the unknown material as being the same as the material with which it matches.

10 Industrial concerns have a need to be able to qualitatively analyze a material to identify the material. For example, when a purchased material has been received, it will normally be identified by labeling and by shipping documents, but these indications are sometimes in error or are missing. By having a system to quickly identify a material when it is received, the material can be identified even if it is mislabeled or the identification of the material is missing before the purchasing company accepts the material and becomes financially responsible for paying for the received material.

15 Prior to the present invention, infrared analysis had been used to qualitatively identify known materials. One such system making use of infrared analysis is described in U.S. Patent No. 4,766,551 to Timothy H. Begley issued August 23, 1988. In the system of the Begley patent, the near infrared (NIR) spectrum of a large number of known products are measured by detecting the absorbance of each known product at incremental wavelengths distributed throughout the NIR spectrum. The measurements at each incremental wavelength making up ℓ measurements are considered to be an orthogonal component of a vector extending in ℓ -dimensional space. The spectrum of the unknown material is also measured and is represented by a vector extending in ℓ -dimensional space. The angle between the vector of the unknown product and the vector of each of the known products is calculated and if the angle between the known product and an unknown product is less than a predetermined minimum, the unknown product is considered to be the same as the known product.

20 The above-described system is reasonably accurate in identifying unknown materials but it takes a substantial amount of time to complete the vector analysis to make the comparison of the unknown product with each known material. Accordingly, this system is not suitable for making a rapid identification of an unknown material such as might be needed on a loading dock.

Summary of the Invention

25 The present invention may be considered an improvement on the system described in the Begley patent and makes it possible to identify unknown materials very quickly.

30 In accordance with the invention, a series of absorbance spectra are measured for a large number of known products. A set of spectra for each known product is determined from different batches of the same product having minor variations, such as might occur from being manufactured by a different process or by having permissible levels of impurities within the product. Each set of spectra comprises absorbance values measured at wavelengths distributed over the near infrared range from 1100 nanometers to 2500 nanometers. The set of spectra for each known product is subjected to principle component analysis to condense the data representing each product to the order of 10 to 20 values or, more specifically, dimensions. The principle component analysis data compression will result in a set of data which will contain about 90 percent or more of the original set of spectra for a given product. The values of the condensed data for a given product are considered to represent a vector, extending in multidimensional or hyperspace and is referred to as a product score vector. Vectors representing the known products are divided into clusters each consisting of vectors close to one another in the hyperspace in which the vectors extend. The vectors all extend from a common origin in hyperspace and the phrase "position of the vector" refers to the position of the end point of the vector in hyperspace. Accordingly, the closeness of the vectors refers to the closeness of the end points of the vectors. A hypersphere, which is a multi-dimensional sphere, is constructed around the position in hyperspace represented by each known product score vector. The radius of the hypersphere will be a scalar quantity times the Euclidean norm determined from the standard deviation spectrum for the product based on the original set of spectra data obtained for the product. By making the scalar multiplier 3, the hypersphere will encompass the positions of 99 percent of the product vectors of all products which are the same as the known product represented by the product vector at the center of the hypersphere. Following the construction of the hyperspheres around each point in space represented by each known product vector, envelopes are constructed around each group of products which are in the same cluster. These envelopes are preferably defined by rectangular coordinates in hyperdimensional space and, accordingly, correspond to a rectangular parallelepiped in three-dimensional space and may be appropriately termed a hyper-rectangular-parallelepiped. For convenience this structure will be referred to as a hyper-box. Each hyper-box will be defined by a minimum and maximum dimension in each of the n-dimensions of the hyperspace.

35 The clustering technique initially divides the vectors representing the known products into clusters having different numbers of vectors in a given cluster. For example, some clusters may have as many as 50 vectors contained therein and other clusters may have only 9 or 10 vectors contained therein or less. When the number of vectors within a cluster exceeds a selected number, for example, between 10 and 20, the vectors within that cluster are divided into child clus-

ters or subclusters by applying principal component analysis to the spectra of the cluster. The child clusters are further divided into grandchild clusters or subclusters to define a hierachial tree of clusters. The division process is carried out until the number of vectors in a given cluster at the most divided level does not exceed the selected number, preferably between 10 and 20. Each of the clusters and subclusters are surrounded by an envelope in the form of a hyper-box. The dimensions of each hyper-box are selected so that it encompasses each hypersphere of each known product vector within the cluster.

When an unknown product is received to be identified, the near infrared spectra of the product is measured yielding absorbance values extending throughout the near infrared range, for example, from 1100 nanometers to 2500 nanometers. This spectral data is processed so as to construct a score vector representing the product, which vector extends in the same space and corresponds to the vectors representing known products. In accordance with the invention, it is first determined whether or not the score vector for the unknown product falls within the envelope of any of the highest order clusters in the hierachial tree. If the vector of the unknown product falls in a cluster which has subclusters, a score vector of the unknown product is then compared with each of these subclusters at the next level in the hierachial tree to determine if the vector of the unknown product falls within the envelope surrounding one of the subclusters. If the vector for the unknown product is then determined to fall into a subcluster which is further divided into subclusters, the process is then repeated at the next level down in the hierachial tree until a score vector of the unknown product is determined to fall into a cluster or subcluster at the lowest level in the hierachial tree. In this manner, the vector will have been determined to be the same as one of the products in the cluster or subcluster at this lowest level of the hierachial tree. Since the subcluster or cluster will have at most 10 to 20 products in the cluster, the number of products to which the unknown product will correspond will have been reduced to 10 to 20 products or less. As indicated above, the number of products in the subcluster may be as few as 2 or may be as many as the selected maximum number between 10 or 20. Following the determination of the final subcluster in which the product falls, an exhaustive comparison is made between the spectrum of the unknown product with the spectra and each known product in the final subcluster to determine which product the unknown product corresponds.

At any point during a process if it is determined that the vector of the unknown product does not fall within any cluster or finally to correspond to any product in the final subcluster, the unknown product is considered to be what is known as an outlier and is determined not to correspond to any of the known products.

The clustering technique described above permits a quick search of the spectra in the library of known products to narrow the number of known products to match the unknown product to a few candidate products in the library. After this quick search by the above-identified process, an exhaustive comparison is made of the library spectra representing just those candidate known products, to which the clustering technique narrowed the search, to positively identify the unknown product as matching one of the known products. This exhaustive comparison on the search involves a relatively time consuming comparison of the spectral data of unknown product with sets of spectral data of the known candidate products to which the search has been narrowed by the clustering technique. Because this comparison is with just a few candidate products, the entire identification process is reduced to a small fraction of the time required by the prior art processes to identify a known product. Yet, because an exhaustive comparison is made of the unknown product with the spectra of the candidate products identified by the clustering technique, the accuracy of the identifying process is very high and is equal to that of the prior art processes.

40 Brief Description of the Drawings

Fig. 1 is a block diagram illustrating the apparatus of the system of the invention;

Fig. 2 is a block diagram of the process representing the known products by vectors and dividing the vectors into a hierachial tree of clusters and subclusters;

45 Fig. 3 illustrates an example of how known products might be divided into clusters by the process of the invention;

Fig. 4 is a schematic illustration of the process of projecting a product mean and standard deviation spectra into principal component inside model space as a score vector and surrounding the score vector with a hypersphere;

50 Fig. 5 is a flow chart representing the process of the system of the invention of comparing an unknown product represented by a vector with the clustered vectors of the known products to determine an identification of the unknown product.

Description of a Preferred Embodiment

The apparatus employed in the system of the present invention comprises a near infrared spectrometer 11 having an oscillating grating 13 on which the spectrometer directs light. The grating 13 reflects light with a narrow wavelength band through exit slit optics 15 to a sample 17. As the grating oscillates, the center wavelength of the light that irradiates the sample is swept through the near infrared spectrum. Light from the diffraction grating that is reflected by the sample is detected by infrared photodetectors 19. The photodetectors generate a signal that is transmitted to an analog-to-digital converter 22 by amplifier 20. An indexing system 23 generates pulses as the grating 13 oscillates and applies these

5 pulses to a computer 21 and to the analog-to-digital converter 22. In response to the pulses from the indexing system 23, the analog-to-digital converter converts successive samples of the output signal of the amplifier 20 to digital values. Each digital value thus corresponds to the reflectivity of the sample at a specific wavelength in the near infrared range. The computer 21 monitors the angular position of the grating 13 and accordingly monitors the wavelength irradiating the sample as the grating oscillates, by counting the pulses produced by the indexing system 23. The pulses produced by the indexing system 23 define incremental index points at which values of the output signal of the amplifier are converted to digital values. The index points are distributed incrementally throughout the near infrared spectrum and each correspond to a different wavelength at which the sample is irradiated. The computer 21 converts each reflectivity value to an absorbance of the material at the corresponding wavelength. The structure and operation of a suitable spectrometer is described in greater detail in U.S. Patent No. 4,969,739.

10 In accordance with the present invention, the instrument shown in Figure 1 is used to measure the absorbance spectra from a large number of known products and stores a library of these spectra in its disc memory. The products from which the library of spectra are obtained are selected to be those which will be likely to correspond to an unknown product to be identified by the system of the present invention. The library of the spectra are subjected to principal component analysis using singular value decomposition. The singular decomposition algorithm is used to determine principal component model space in order to reduce the number of values representing the spectrum of each product in the library of products.

15 In accordance with the invention, several different samples of each product for the library are obtained and each of the different samples of a given product are selected to have minor variations from each other such as would occur from being provided by different manufacturers or being produced by different manufacturing processes.

20 The system of the invention shown in Fig. 1 is used to measure and obtain an absorbance spectrum of each sample of each product thus providing a plurality of spectra for each product. Each spectrum is measured at the same incremental wavelengths.

25 The several spectra for the different samples or a product in the library is called a training set. If there are n samples of a given product so that there are n spectra in a training set for a product, then the spectrum of one sample in the training set can be represented as follows:

$$x_i = [x_{i1}, x_{i2}, \dots, x_{i\ell}]^T \quad (1)$$

30 in which x_i is a column vector made up of reflectance measurements x_{i1} through $x_{i\ell}$ taken from the sample i at each of the incremental wavelength points 1 through ℓ . In accordance with the invention, the computer determines a mean spectra from each product training set by averaging the reflectivity values of the training set at each wavelength to thus determine a mean spectra for the product which can be represented as follows:

$$x^m = \frac{1}{n}(x_1 + x_2 + \dots + x_n) \quad (2)$$

40 In the above equation x^m is a column vector of the mean spectrum values and x_1 to x_n are each column vectors representing the spectrum of each of the samples 1 through n .

45 As described in the above-mentioned Begley patent, each known product may be represented by a multidimensional vector extending in hyperspace wherein each dimension of the vector is defined as a different one of the absorbance measurements distributed throughout the spectrum. Typically, the near infrared spectrum is measured by 700 incremental measurements distributed throughout the spectrum so that in the system of the Begley patent, each known product will be represented by a 700 dimensional vector.

50 In the system of the present invention, to reduce the computation required and thereby reduce the amount of time to make the computation to identify the products, the spectra of the products are subjected to principal component analysis. This process reduces the number of numerical values representing each product so that each product may be represented by a vector extending in hyperspace of substantially fewer dimensions, e.g. 10 to 20 dimensions. To carry out the principal component analysis, first a global principal component model space is determined from the mean spectra representing the library of known products. As a first step of this process, the column vectors of the mean spectra are considered to form a matrix X as follows:

$$55 X = (x^m_1, x^m_2, \dots, x^m_n) \quad (3)$$

In this expression x^m_1 through x^m_n each represents a column vector of a mean spectrum for a different one of the products in the product library of known products 1 through n . This expression for the mean spectral matrix of the product library is simplified by dropping the superscript as follows:

$$X = (x_1, x_2, \dots, x_n) \quad (4)$$

From the spectra x_1 through x_n a mean column vector \bar{x} is determined by averaging the values in the spectral matrix X at each wavelength. Since X is spectral matrix of mean vectors, the mean vector \bar{x} will actually be a mean vector of a set of mean vectors which is determined from the vectors in the matrix X of Equation 3 as follows:

$$\bar{x} = \frac{1}{n}(x_1 + x_2 + \dots + x_n) \quad (5)$$

wherein x_1 through x_n are mean vectors representing the different products in the spectral library. The vector \bar{x} thus represents an average absorbance at each wavelength from these mean vectors representing the known products. From the global mean vector \bar{x} , a mean centered matrix \bar{X} is calculated as follows:

$$\bar{X} = (x_1 - \bar{x}, x_2 - \bar{x}, \dots, x_n - \bar{x}) \quad (6)$$

Each of the expressions $(x_1 - \bar{x})$ through $(x_n - \bar{x})$ is a column vector and each column vector is determined by subtracting the global mean vector \bar{x} from each of the product mean vectors x_1 through x_n . Singular value decomposition is then applied to the mean centered matrix \bar{X} to obtain

$$\bar{X} = UWV' \quad (7)$$

in which U is an ℓ by n matrix of orthonormal vectors, V' is an n by n matrix of orthonormal vectors and W is an n by n diagonal matrix. The diagonal elements of W are

$$w_1 \geq w_2 \geq \dots \geq w_n \geq 0 \quad (8)$$

and are singular values of \bar{X} . The values w_1 through w_n are defined as the square root of the eigenvalues of the covariance matrix $\bar{X}'\bar{X}$ wherein \bar{X}' is the transpose of \bar{X} . The eigenvalues of the covariance matrix $\bar{X}'\bar{X}$ corresponding to the squares of w_1 through w_n are represented as λ_1 through λ_n . The principal components of the mean centered spectral data matrix \bar{X} are the eigenvectors of the covariance matrix $\bar{X}'\bar{X}$, which are associated with the nonzero eigenvalues. The column vectors of U in the Expression 7 which are associated with nonzero eigenvalues are these eigenvectors and are the principal components for the mean centered spectral matrix \bar{X} . Since there are n different mean centered product spectra making up the column vectors of \bar{X} , there are n column vectors in the mean centered matrix \bar{X} and there exist $n-1$ nonzero singular values of \bar{X} . Accordingly, there are $n-1$ principal components of the matrix \bar{X} . The Expression 7 can be rewritten in the following standard form in principal component analysis:

$$\bar{X} = LS \quad (9)$$

in which L is an ℓ by $n-1$ matrix expressed as follows:

$$L = [u_1, u_2, \dots, u_{n-1}] \quad (10)$$

In the matrix L , u_1 through u_{n-1} are column vectors and comprise the principal components of the mean centered matrix \bar{X} . The matrix L is referred to as the loading matrix.

In Equation (9) S is an $n-1$ by n matrix called the score matrix and is represented as follows:

$$S = \text{diag}(w_1, w_2, \dots, w_{n-1})[v_1, v_2, \dots, v_{n-1}]' \quad (11)$$

The principal component vectors of the matrix L span a multidimensional space or hyperspace called principal component model space of the mean centered spectral matrix \bar{X} . While as represented in the matrix L , the principal components (vectors) are normalized, the vector lengths are of no significance. It is the direction of the principal components in representing the coordinates of the principal component model space that is significant. Each of the column vectors in the mean centered spectral matrix \bar{X} can be projected in principal component model space and represented as a linear combination of coordinate values.

The magnitude of the eigenvalues λ_1 through λ_{n-1} are proportional to the amount of variance in the mean centered spectral data matrix \bar{X} which are modeled by the corresponding principal components represented by the column vectors u_1 through u_{n-1} of the matrix L . The principal components associated with the largest eigenvalues model the largest

fraction of the total variance in \bar{X} . It is possible to model most of the variance in the spectral matrix \bar{X} by substantially fewer than $n-1$ principal components. The set of nonzero eigenvalues can be partitioned in two sets, a primary set λ_1 through λ_k , and a secondary set λ_{k+1} through λ_{n-1} . The primary set includes all values substantially greater than zero so that the secondary set have minimum values substantially equal to zero. The primary set of eigenvalues will cover a large percentage of the cumulative variance of the mean centered spectral matrix \bar{X} . In the same way the loading matrix L can be partitioned into L_1 and L_0 wherein L_1 is a matrix made up of the column vectors u_1 through u_k called the primary principal components and L_0 is a matrix made of the column vectors u_{k+1} through u_{n-1} which are referred to as the secondary principal components. Equation (9) can be rewritten as:

$$10 \quad \bar{X} = L_1 S_1 + L_0 S_0 \quad (12)$$

In this equation, S_1 , which is a k by n matrix, can be expressed by following:

$$15 \quad S_1 = \text{diag } (w_1, w_2, \dots, w_k) [v_1, v_2 \dots v_k]' \quad (13)$$

and S_0 , which is an $n-k-1$ by n matrix, can be represented as follows:

$$S_0 = \text{diag } (w_{k+1}, w_{k+2}, \dots, w_{n-1}) [v_{k+1}, v_{k+2} \dots v_{n-1}]' \quad (14)$$

20 The set of primary principal component vectors represented by u_1 through u_k define the orthonormal basis of what is referred to as inside model space of the mean centered spectral matrix \bar{X} . The set of secondary principal components represented by v_{k+1} through v_{n-1} define the orthonormal basis of what is defined as outside model space. Each spectrum represented by the column vectors of \bar{X} can be decomposed into the sum of two vectors. The first vector projects in the inside model space and represents the most significant correlated behavior of the vectors in principal component model space, since w_1 through w_k covers most of the variance in \bar{X} . The second vector projects in outside model space, represents the residual variations in the principal component model space, and is considered to be random error. The second vectors projecting in outside model space are omitted from the analysis because they represent noise and other error terms. The primary principal component vectors u_1 through u_k provide an orthonormal basis for K -dimensional inside principal component space which describes most of the variation in the original mean center spectral data matrix \bar{X} . The corresponding score matrix $S_1 = [s_1, s_2, \dots, s_n]$ can be computed by

$$30 \quad S_1 = L_1' \bar{X} \quad (15)$$

35 in which L_1' is the transpose of L_1 . The vectors s_1 through s_n are each column vectors having k dimensions and are the principal component scores for the corresponding vectors $x_1 - \bar{x}$ through $x_n - \bar{x}$ of the mean centered spectral data matrix in principal component inside model space. In other words, when one of the vectors $x_i - \bar{x}$ is projected in principal component inside model space the values of its coordinates are represented by the column vector s_i . The principal component score vector for each mean centered spectrum $(x_i - \bar{x})$ can be directly calculated by

$$40 \quad s_i = L_1' (x_i - \bar{x}) \quad (16)$$

The above equation gives a linear transformation in which a spectrum represented by a vector having ℓ dimensions is transformed to a score vector in the principal component inside model space. In this manner, each of the column vectors in this mean centered matrix \bar{X} is transformed into a vector in principal component inside model space having substantially fewer dimensions than the original vector.

50 Principal component analysis is a known statistical data compression technique and is described in the text entitled *Factor Analysis* by Malinowski. By the process described thus far the entire or global set of mean vectors representing the known products are processed by principal component analysis to yield set of score vectors projected into principal component inside model space. Since each score vector represents a known product, they are referred to as known product score vectors. This process represented in the flow chart of Figure 2 as step 31 in which the global set of spectra of mean vectors representing known products is transformed into a mean centered matrix \bar{X} and step 33 in which the mean centered matrix is subjected to principal component analysis to yield the known product score vectors for the matrix determined in step 31. These vectors, which each correspond to a different one of the products in the library of products, are then separated into clusters in step 35. To determine which known product score vectors will be in which cluster, the Euclidean distance between the end point of each known product score vector and each other known product score vector is measured and a minimal spanning tree is constructed linking the vectors. The minimal spanning tree is then used to separate the vectors into clusters by dividing the minimal spanning tree at those links of the minimal

spanning tree which have the greatest lengths. More specifically, the average length of the minimal spanning tree link is determined and the standard deviation in the length of the minimal spanning tree links is also determined. The minimal spanning tree is then separated into clusters of vectors by defining a cluster separation at each minimal spanning tree link which is greater in length than the average minimal spanning link plus a scaling factor times the standard deviation in the lengths of the minimal spanning tree links expressed as follows:

$$a + k\delta,$$

wherein a is the average length of a minimal spanning tree link, k is the scaling factor and δ is the standard deviation in the length of the spanning tree link.

This process will thus divide the product score vectors from the entire library of products into a set of clusters.

Typically, most of the clusters will contain more than the permitted maximum product score vectors and these clusters are further divided into clusters by repeating the process limited to the products of each cluster. Thus in step 37, if the permitted maximum number of vectors in an individual cluster is 10, it is determined whether any of the cluster have more than 10 vectors. If so, the process proceeds into step 39 in which mean centered matrices are determined for the large clusters containing more than 10 vectors, a separate matrix being determined for each large cluster from the corresponding mean vectors representing the corresponding known products. The process then loops back through step 33 to perform the principal component analysis on the mean centered matrices determined from the large clusters. This process determines a set of principal components for each large cluster to be subdivided and then determines a principal component inside model space for each large cluster. Following this determination the process proceeds again through step 35 to divide vectors of each large cluster into subclusters in the same manner as described above. In this subdivision process, the vectors being subdivided will be closer together than in the first iteration through step 35 so the average length of the minimal spanning tree links between product vectors will be smaller and the criteria for separating the vectors into subclusters will therefore be finer. The principal component analysis as described above is thus carried out to further divide the large clusters containing more than permitted maximum number of product vectors into additional clusters called subclusters or child clusters. In a similar manner the child clusters are then further divided into grandchild clusters, and great grandchild clusters, and great, great grandchild clusters, if necessary, until each cluster or subcluster contains no more than ten products.

An example of this clustering technique is illustrated in Figure 3. In this figure the library of products is assumed to contain 150 known products and in the example illustrated the first division of these products into clusters divides them into a cluster of two, a cluster of 25, a cluster of 38, a cluster of 33, a cluster of nine, and a cluster of 43 products. In this example, the maximum number of vector permitted to be in cluster not to be further subdivided is selected to be ten. The clusters of 25, 38, 33 and 43 having more than ten products need to be divided into further subclusters because they contain more than ten products and accordingly the cluster containing 25 products is divided into subclusters or child clusters which in this example are represented as containing three, seven, and 15 products, respectively. The subcluster containing 15 products is then further divided into subclusters or grandchild clusters containing five and ten products, respectively. The highest level cluster containing 38 products in the example is shown as being divided into subclusters or child clusters containing 15, 17 and seven products, respectively. The child cluster containing 15 products is then further divided into clusters containing ten and five products, respectively, at the third level, and the child cluster containing 17 products is further divided into grandchild clusters containing 12 and five products, and the grandchild cluster of 12 products is further divided into great grandchild clusters containing four and eight clusters at the fourth level. The remaining initial clusters containing 33 and 43 are similarly further divided. In the illustration, the cluster division goes to four levels or great grandchild clusters, but theoretically there is no limit to how many levels the clusters may be further subdivided.

When all of the large clusters have been subdivided into subclusters the process proceeds from step 37 into step 41. In this step a hypersphere is constructed around each vector in each cluster, including the parent clusters as well as the subclusters. The hypersphere will have the same number of dimensions as the principal component inside model space in which it is constructed and therefore will be k -dimensional. The radius of each hypersphere is determined from the Euclidean norm of the standard deviation spectrum of the training set of spectra for the corresponding product multiplied times a scalar factor which may be selected by the user. To calculate the Euclidean norm of the standard deviation spectrum of a training set, the standard deviation is calculated from the training set values at each wavelength measurement point distributed throughout the spectrum and then the Euclidean norm is calculated from these values by taking the square root of the sum of the squares as follows:

$$r = \left(\sum_{i=1}^t x_i^s \right)^{1/2} \quad (17)$$

in which r is the radius and x_s^s is the standard deviation of the training set absorbances at measurement point i . Typically the scalar factor will be selected to be three so that 99% of vectors derived from products corresponding to the product of the training set would be represented by a vector falling within the hypersphere.

5 The above described process is illustrated in Fig. 4. In this illustration the product mean spectrum x^m_i yields a mean centered spectrum $x_i - \bar{x}$, which is projected as a product score vector s_i into principal component inside model space by the operation $L'_1(x_i - \bar{x})$. A hypersphere having a radius equal to the Euclidean norm of the standard deviation spectrum of the training set of absorbance spectra for the product multiplied times the scalar factor is constructed around the product score vector s_i .

10 Following the generation of the hyperspheres, envelopes are constructed in step 43 around each cluster of products and each subcluster of products. The envelopes are in the form of multidimensional rectangular boxes called hyper-boxes having the same number of dimensions as the principal component inside model space (k dimensions), and will be constructed so as to encompass each of the vector end points and their surrounding hyperspheres.

15 The process of identifying an unknown product is illustrated in Figure 5. In this process, first a quick search of the library known spectra is conducted using the clusters defined as described above. In the quick search, the absorbance spectrum from the unknown product is obtained and a score vector of the resulting spectrum is projected into the principal component inside model space constructed for the global set of clusters in the first step of dividing the clusters. To carry out this projection, first the global mean vector \bar{x} has to be subtracted from the vector representing the unknown product, then the resultant mean corrected vector representing the unknown product is multiplied by the projection operator L'_1 wherein L_1 and L'_1 have been calculated as described above. The projection operator L'_1 projects the 20 unknown sample spectrum as a score vector in the principal component inside space spanned by the global principal component vectors. After the projection of the unknown sample into the principal component inside space of the global set of mean vectors, the process determines whether or not the resulting projected product vector representing the unknown product falls within any of the hyper-box envelopes surrounding the clusters. If the vector representing the unknown product falls within the envelope of a cluster, that is one that is not further subdivided, the identification process 25 then proceeds with the exhaustive search comparing the unknown product with each of the products in the cluster, as will be described below.

25 If the unknown product vector falls in a cluster which is further divided into subclusters, then the above-described process must be repeated for the subclusters to determine which of the subclusters a vector representing the unknown product falls into. As explained above, the principal component inside model space for dividing each cluster into subclusters is different than the global principal component inside model space determined for the global set of mean vectors and also different from that determined for other subclusters. Accordingly, the process of calculating the projection of the unknown product into principal component inside model space must be carried out separately for each subcluster. Thus, in carrying out the projection for given subcluster, the mean vector of the mean centered matrix for the parent cluster will be subtracted from the unknown product vector to determine the mean corrected vector representing the unknown product. Then this mean corrected spectrum vector is multiplied by the projection operator L'_1 for the relevant principal component inside model space to project the mean corrected unknown product vector into this principal component inside model space. The relevant principal component inside model space will be that hyperspace used to divide the parent cluster into subclusters. This process is repeated until the vector representing the product is found to fall in a subcluster which is not further divided or otherwise found to fall outside of any subcluster.

40 When the cluster identification step of the process has been completed and the unknown product is found to fall into an identified cluster or subcluster which is not further divided, an exhaustive search is conducted on the library spectra of those known products of that identified cluster or subcluster to determine which product the unknown product corresponds with. This determination may be carried out by several different methods, one of which is the method described in the above-mentioned patent to Begley wherein the angle between the multidimensional vector represented by the product spectra is compared with the angles of the mean vectors representing the products in the same cluster and if the cosine of the angle between the vectors is less than a certain selected minimum, the product is deemed to be the same product.

45 A second method is to compare the spectrum of the unknown product point by point with a spectrum band determined from each training set of spectra representing one of the products in the cluster. The spectrum band is determined by calculating the standard deviation of the training set at each wavelength measurement to determine an upper and lower limit for the band at each wavelength. The upper and lower limit is $x^m_i \pm \beta x_s$, in which x_s represents the standard deviation at each wavelength and β represents a scalar quantity selected by the user. An example of such a band is illustrated in Figure 4. The product is determined to be the same as a specific product in the cluster if every point in its absorbance spectrum falls within the band determined from the training set spectra extending over the near infrared of measurement.

50 In accordance with a third method of performing an exhaustive search of the library spectra of the products corresponding to the cluster identified in the quick search, principal component analysis is applied to each training set of spectra for each product corresponding to the identified cluster. This determination yields a model of principal component inside space for the training set of each product of the cluster. To match the unknown sample with a known product,

the score vector from the unknown sample in the local principal component inside model space is determined and the Mahalanobis distance of the score vector and the mean of the score vectors of the training set is calculated. If the Mahalanobis distance of the score vector of the unknown sample is less than the threshold value selected by the user, the unknown sample is determined to match the known sample of the local principal component inside model space. The Mahalanobis distance between the score vector and the mean of the training set score vectors of a known product can be determined from the sum of the squares of the coordinates of the unknown product of the score vector weighted by the associated eigenvalues as follows:

$$10 \quad d_M^2(s) = (n-1) \sum_{j=1}^k (s_j^2 / \lambda_j)$$

in which $d_M^2(s)$ represents the Mahalanobis distance, n is the number of samples in the training set, s_j is the j^{th} coordinate of the score vector of the unknown sample, and λ_j is the j^{th} eigenvalue associated with the local principal component inside model space derived from the training set of the known product. Geometrically, all score vectors at a Mahalanobis distance smaller than a constant will fall within an ellipsoid boundary in local principal component inside model space centered on the mean of the score vectors of the training set.

Each of the above-described methods of product identification is satisfactory with the first described method of the Begley patent taking the shortest amount of time, the second method taking more time and the third method taking still more time to complete the matching of the unknown product with the known product. Accordingly, in accordance with the preferred embodiment the three methods are carried out in sequence with the method of the Begley patent being used to rule out a first group of the products of the cluster, leaving a remaining smaller group to be considered and then the second method being used to rule out a subgroup of this second smaller group, leaving a third still smaller group to be considered, and then using the Mahalanobis distance method to perform the final matching of the unknown product with a known product in the product library.

As described above, the process employs principal component analysis to reduce the dimensions of the vectors representing both the known products and the unknown products for comparison of the vectors with the clusters of hyperspheres. It will be apparent that the process could be performed without using principal component analysis and simply comparing the mean product vectors representing each product training set by a vector extending in hyperspace having dimensions equal to the number of spectral measurements throughout the infrared range and clustering the products and comparing the unknown products with the cluster of products in the same manner essentially as described above. In addition, other methods instead of principal component analysis may be used to compress the dimensions of the vectors representing each product.

Because the above-described clustering technique is used and also because it is used in combination with the principal component analysis to reduce the number of dimensions of the vectors, the time required to match a product with an unknown product in the library is reduced to a small fraction of the time required by the prior art methods. Accordingly, the system may be used on a loading dock to quickly determine the contents of a received product before a newly delivered product is accepted.

The above description is of a preferred embodiment of the invention and modification may be made thereto without departing from the spirit and scope of the invention which is defined in the appended claims.

Claims

1. A method of matching an unknown product with one of a library of known products comprising the following steps:

45 step (1): measuring a near infrared absorbance spectrum for each of said known products,
 step (2): generating known product vectors extending into hyperspace representing the absorbance spectra determined for each of said known products,
 50 step (3): dividing said known product vectors into clusters of vectors extending into hyperspace wherein the vectors each cluster are closer to each other in hyperspace than the vectors outside of such cluster,
 step (4): dividing at least some of said clusters of vectors into subclusters of vectors extending into hyperspace,
 55 step (5): repeating said step (4) on at least some of said subclusters until all of said subclusters have fewer than a predetermined number of vectors,
 step (6): surrounding each of said clusters and subclusters with an envelope defined in the corresponding hyperspace,
 step (7): measuring the absorption spectrum of said unknown product,
 step (8): determining in which of said envelopes surrounding said clusters divided in step (3) a vector, representing said unknown product and extending into the hyperspace of said clusters, falls,
 step (9): if the vector representing said unknown product falls into an envelope surrounding a cluster which is

divided into subclusters, then determining in which envelope surrounding a subcluster a vector representing said unknown product and extending into the hyperspace of such subcluster, falls,

step (10): repeating the step (9) on further divided subclusters until a vector representing said unknown product is determined to fall into an envelope surrounding a subcluster which is not further divided,

5 step (11): then determining which known product represented by a vector within said last-named envelope said unknown product matches.

2. A method as recited in claim 1 wherein said step (2) includes subjecting said absorbance spectra determined of said known products to principal component analysis to determine a known product score vector representing each known product projected into principal component inside model space.

10 3. A method as recited in claim 2 wherein said step (4) includes subjecting the absorbance spectra of the known product vectors of each cluster and subcluster to principal component analysis to determine a product score vector for each known product of the cluster or subcluster extending into principal component inside model space determined for the known product spectra of such cluster or subcluster.

15 4. A method as recited in claim 2 further comprising surrounding each known product score vector with a hypersphere, said step (6) including surrounding the hyperspheres of the corresponding clusters with each of said envelopes.

20 5. A method as recited in claim 2 wherein each of said envelopes comprises a hyperbox of orthogonal dimensions.

6. A method as recited in claim 1 further comprising surrounding each of said known product vectors with a hypersphere, said step (6) including surrounding the hyperspheres of the corresponding clusters with said envelopes.

25 7. A method as recited in claim 1 wherein each of said envelopes comprises a hyperbox having orthogonal dimensions.

8. A method of matching a product with one of a library of known products comprising

30 measuring the absorbance spectra of said known products,
subjecting said absorbance spectra to principal component analysis to determine known product score vectors projecting in principal component inside model space,
surrounding said known product score vectors with hyperspheres,

35 measuring the absorbance spectrum of said unknown product,
determining from the spectrum of said unknown product an unknown product score vector projecting in principal component inside model space, and
determining in which of said hyperspheres said unknown product score vector falls.

40 9. A method as recited in claim 8 wherein said absorbance spectra of said known products includes a training set of a plurality of spectra for each of said known products and wherein said method includes obtaining an average absorbance spectra of each training set, determining from said average spectra and the corresponding training set a standard deviation for each known product, the hyperspheres each having a radius equal to a selected multiple of said standard deviation.

45

50

55

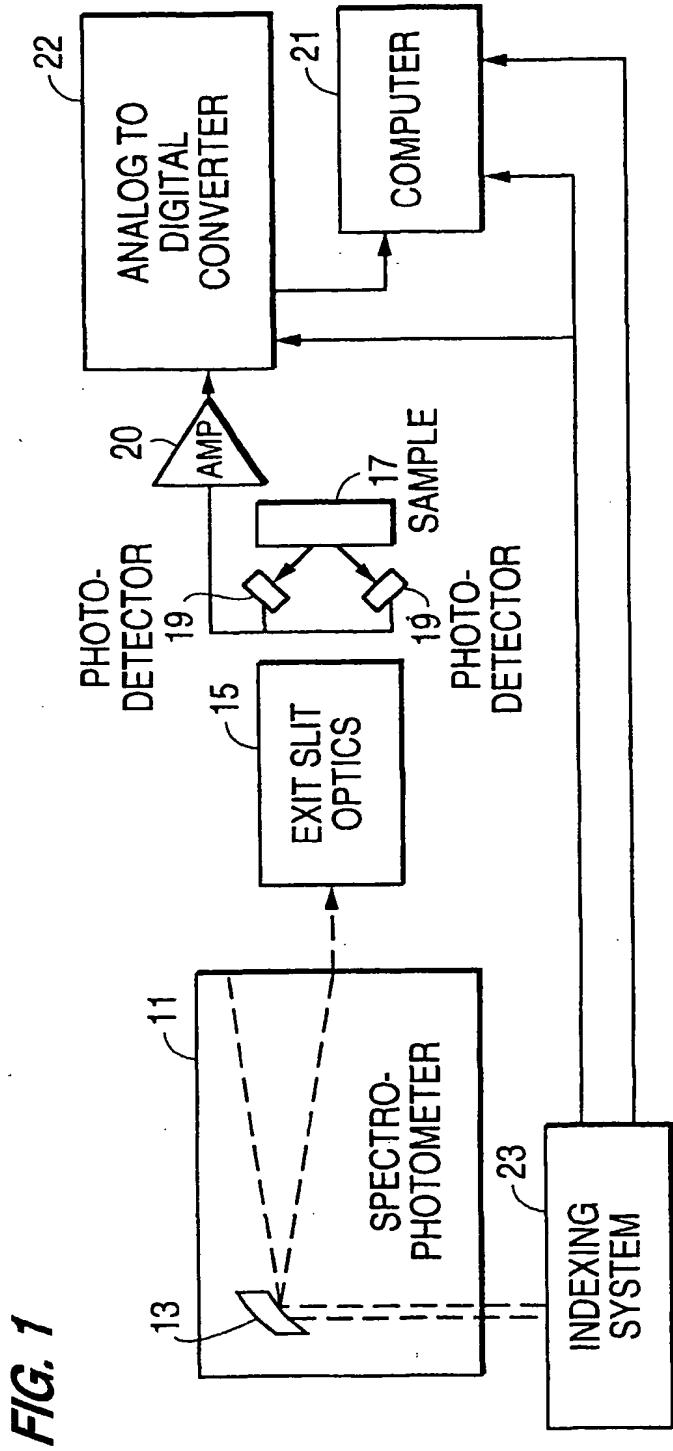


FIG. 2

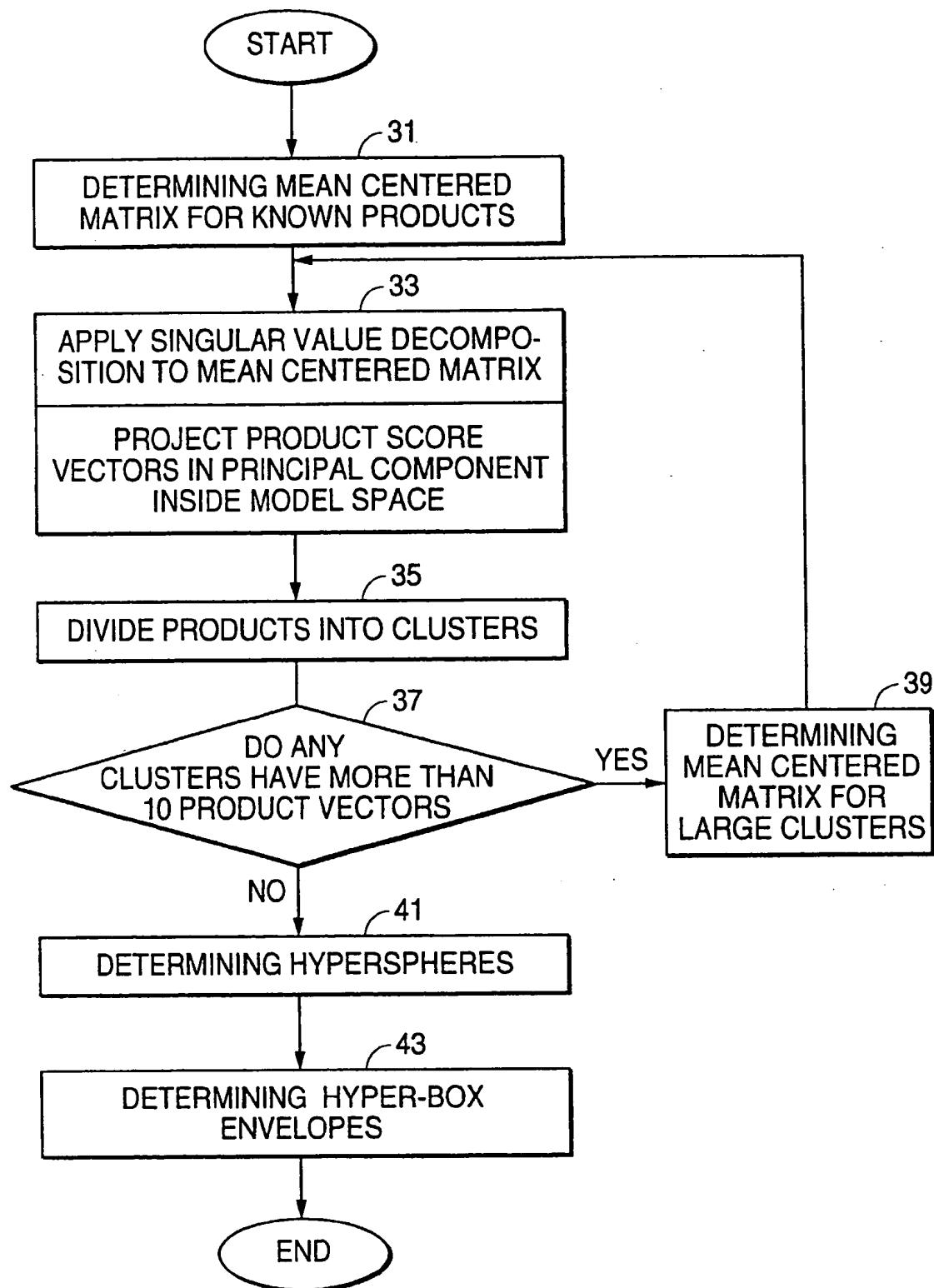


FIG. 3
KNOWN PRODUCT
SPECTRA

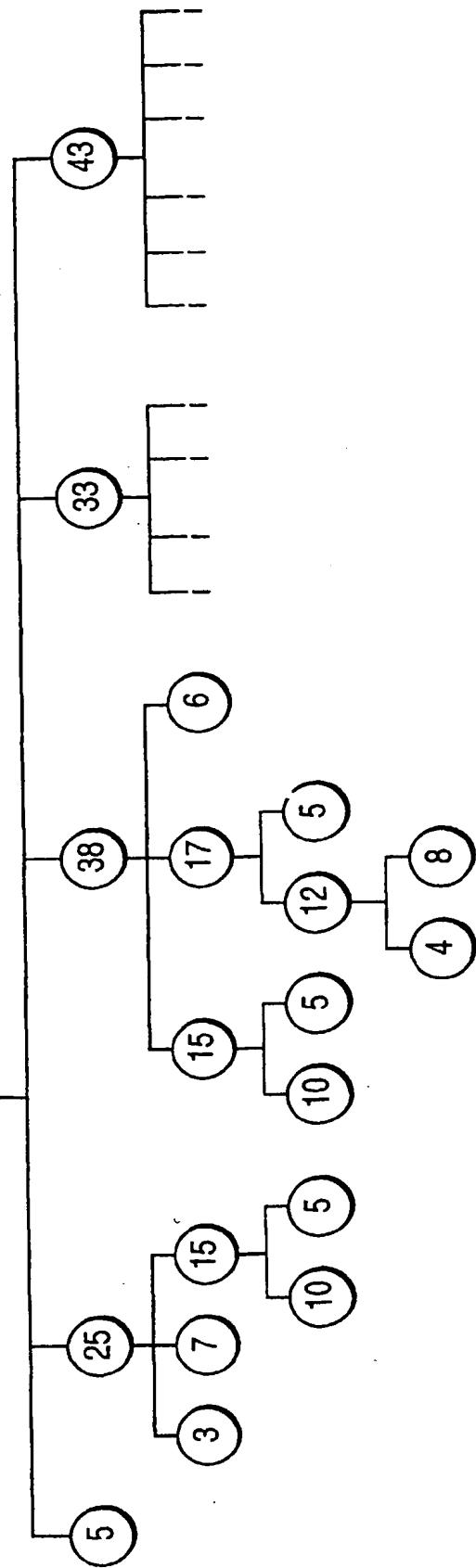


FIG. 4

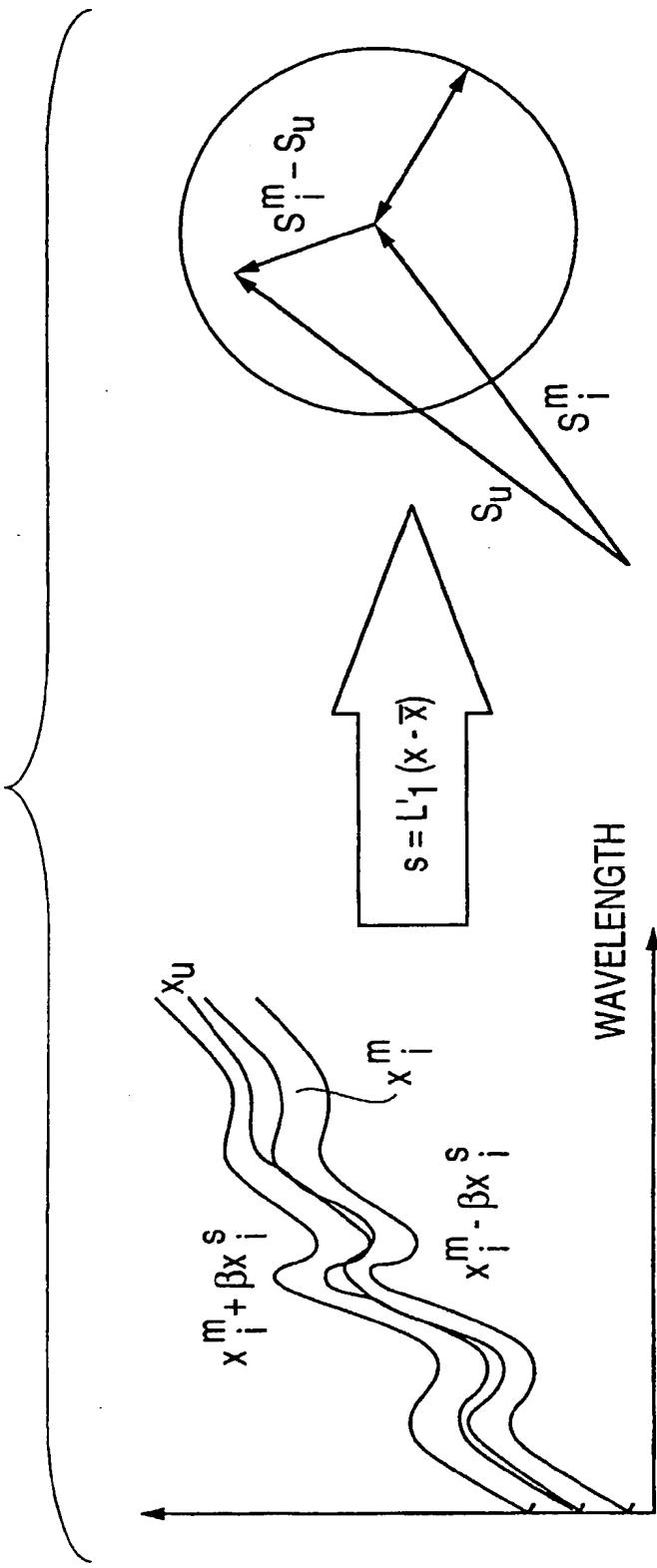
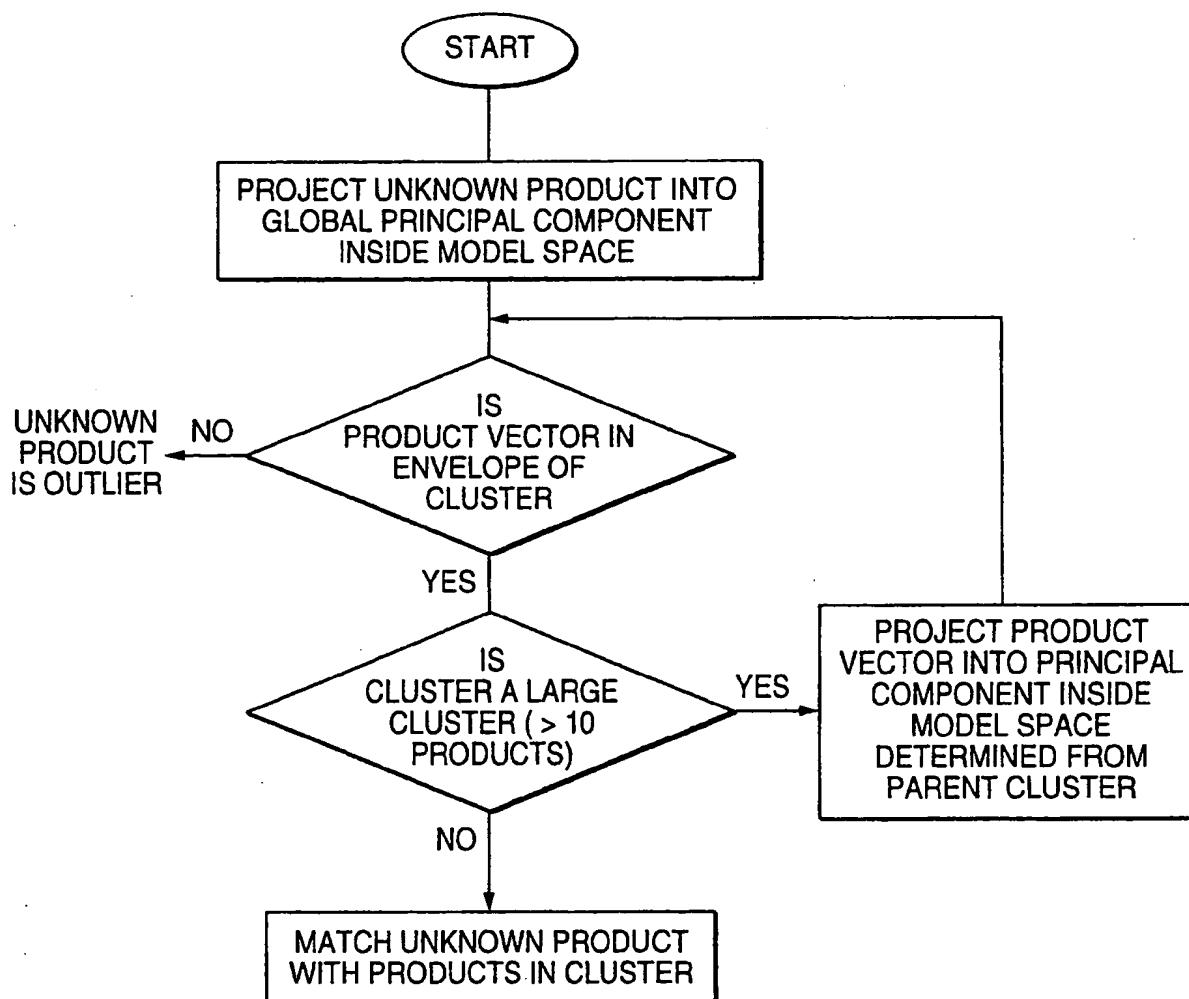


FIG. 5



(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11)

EP 0 807 809 A3



(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
01.07.1998 Bulletin 1998/27

(51) Int. Cl.⁶: G01N 21/35

(43) Date of publication A2:
19.11.1997 Bulletin 1997/47

(21) Application number: 97107518.9

(22) Date of filing: 07.05.1997

(84) Designated Contracting States:
DE FR GB

(30) Priority: 13.05.1996 US 645104

(71) Applicant:
Perstorp Analytical, Inc.
Silver Spring, Maryland 20904 (US)

(72) Inventors:
• Chen, Xiaolin
Elkridge, Maryland 21227 (US)
• Monfre, Stephen L.
Plainville, Massachusetts 02762 (US)

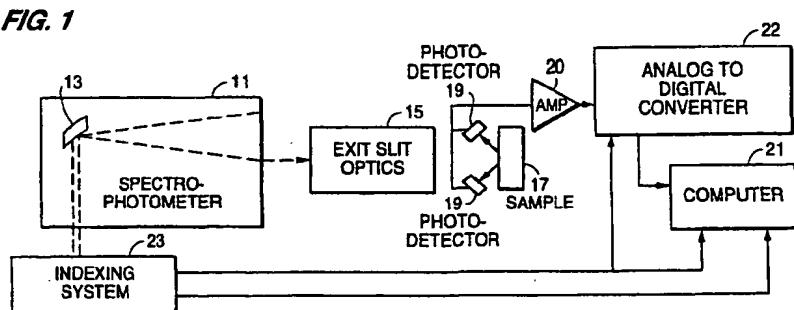
(74) Representative:
DIEHL GLAESER HILTL & PARTNER
Patentanwälte
Königstrasse 28
22767 Hamburg (DE)

(54) System for identifying materials by NIR spectrometry

(57) In a method for identifying an unknown product a library of absorbance spectra of known products is measured and stored in a library. A quick search using clustering techniques is conducted to narrow the search to a few products, followed by an exhaustive search of the spectra of the few products. More specifically, principal component analysis is applied to the absorbance spectra to generate product score vectors extending into principal component inside model space which are divided into clusters and subclusters in accordance with their relative proximity. Hyperspheres are constructed around each vector and an envelope is constructed to enclose each cluster surrounding the hyperspheres within the cluster. The absorbance spectrum of the unknown product to be identified is measured and an unknown product score vector is determined from the

unknown product spectrum projecting in principal component inside model space of the clusters. It is determined whether or not the unknown product score vector falls within one of the envelopes and if so the product score vector is projected into the principal component inside model space of that cluster and it is determined whether or not the unknown product score vector falls within any of the subclusters divided from the cluster. This process is repeated until the unknown product score vector is found to lie in a cluster which is not further subdivided. In this manner, the search is narrowed to a few products. An exhaustive search is then carried out to match the spectrum of the unknown product with the spectra of the known products corresponding to the undivided subcluster.

FIG. 1



EP 0 807 809 A3



EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 97107518.9
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
A	<u>US 5397899 A</u> (DIFOGLIO) 14 March 1995 (14.03.95), abstract, claims. --	1, 8	G 01 N 21/35
A	<u>US 5508525 A</u> (DAY) 16 April 1996 (16.04.96), abstract, claims, fig. 4. --	1, 8	
A, D	<u>US 4766551 A</u> (BEGLEY) 23 August 1988 (23.08.88), abstract, claims, column 2, line 54 - column 3, line 40, fig. 1-3. --	1, 8	
A	<u>EP 0535700 A2</u> (THE PERKIN-ELMER CORP.) 07 April 1993 (07.04.93), abstract, claims. --	1, 8	
A	<u>WO 90/11507 A1</u> (THE LUBRIZOL CORP.) 04 October 1990 (04.10.90), abstract, claims. --	1, 8	G 01 J 3/00 G 01 N 21/00
A	<u>WO 85/01348 A1</u> (BECKMANN INSTR.) 28 March 1985. (28.03.85), abstract, claims, fig. 1-8. -----	1, 8	
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search		Examiner
VIENNA	31-03-1998		ERBER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER: _____**

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.